

**LAUNDRY TREATMENT COMPOSITIONS AND COMPONENTS THEREFOR**

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**Technical Field**

The present invention relates to compositions for softening textile fabrics and which also contain a perfume and a deposition aid..

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**Background of the Invention**

Silicones of various structures are well known as ingredients of rinse conditioners to endow softness to fabrics.

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WO 03/015736 discloses an aqueous skin-care, hair-care or fabric-care composition which comprises a surfactant, a silicone which is insoluble in water, and a perfume having a solubility parameter not exceeding about 20. The composition preferably includes a deposition aid, e.g. a cationic deposition aid, to enhance deposition. One preferred class of materials is cationic guar gum derivatives such as guar hydroxypropyltrimmonium chloride (which is commercially available from Rhodia under the Trade Mark Jaguar). Particularly preferred is Jaguar C13S, which has a low degree of substitution of the cationic groups and high viscosity, and this is the only compound identified as a deposition aid in the specific examples of WO 03/015736.

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WO 02/18528 discloses systems, compositions and methods for domestic laundering comprising selected cationic silicone polymers formulated for improved fabric care. In a preferred method for preparing the compositions, it is revealed that the cationic silicone polymer may be mixed with fabric substantive perfume ingredients to form a cationic silicone polymer premix.

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Our UK patent application no. 0121148.1, unpublished at the priority date of this invention, describes and claims a substituted  $\beta_{1,4}$  linked polysaccharide having covalently bonded on the polysaccharide moiety thereof, at least one deposition enhancing group which undergoes a chemical change in water at a use temperature to

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increase the affinity of the substituted polysaccharide to a substrate, the substituted polysaccharide further comprising one or more independently selected silicone chains. The polysaccharide acts as a vehicle to deposit the silicone chains bound to it, onto the fabric, from a wash liquor.

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Further, our UK patent application no. 0123380.8, also unpublished at the priority date of this invention also discloses that such substituted polysaccharides can be incorporated in compositions containing a silicone *per se* to enhance deposition of the free silicone.

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When a silicone is delivered as a fabric softening agent in a fabric conditioner in the rinse cycle, consumers greatly appreciate the deposition of a perfume from the fabric conditioner as this gives a pleasing sensation in combination with the resultant softness and smooth feel of the fabric. However, in principle, a silicone does not strictly have to be dosed from a fabric conditioner in the rinse cycle and could for example be delivered in a main wash product. This reduces the amount of perfume which would be carried through to the dried fabric after rinsing and drying. However, we have now discovered that this problem may be overcome by incorporating a perfume component into the silicone. This is especially (but not exclusively) beneficial when the silicone is delivered to the fabric using a deposition aid such as the substituted polysaccharide referred to above, which is primarily intended to deliver a softening benefit from silicone materials in the wash.

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### **Definition of the Invention**

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A first aspect of the present invention provides a composition (e.g. a chemical composition or a laundry treatment composition) comprising a silicone and a deposition aid, for example a substituted polysaccharide comprising  $\beta$  1,4 linkages having covalently bonded on the polysaccharide moiety thereof, at least one deposition enhancing group which undergoes a chemical change in water at a use temperature to increase the affinity of the substituted polysaccharide to a substrate, the substituted polysaccharide further comprising one or more independently selected silicone chains, the composition further comprising a perfume component dissolved or dispersed in the silicone.

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A second aspect of the present invention provides a method for depositing a silicone onto a substrate, the method comprising, contacting in an aqueous medium, the substrate and a composition according to the first aspect of the invention.

- 5 A third aspect of the invention provides the use of a composition according to the first aspect of the invention to enhance the softening benefit of a laundry treatment composition on a substrate.

### **Detailed Description of the Invention**

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#### **THE SILICONE**

As used herein reference to a silicone in which a perfume component is dispersed or dissolved therein includes both a single liquid silicone compound or a mixture of two or  
15 more different liquid silicone compounds.

Silicones are conventionally incorporated in laundry treatment (e.g. wash or rinse) compositions to endow antifoam, fabric softening, ease of ironing, anti-crease and other benefits. Any type of silicone can be used to impart the lubricating property of the  
20 present invention however, some silicones and mixtures of silicones are more preferred.

Typical inclusion levels are from 0.01% to 25%, preferably from 0.1% to 5% of silicone by weight of the total composition.

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Suitable silicones include :

- non-volatile silicone fluids, such as poly(di)alkyl siloxanes, especially polydimethyl siloxanes and carboxylated or ethoxylated variants. They may be branched, partially  
30 cross-linked or preferably linear.
- aminosilicones, comprising any organosilicone having amine functionality for example as disclosed in EP-A-459 821, EP-A-459 822 and WO 02/29152. They may be branched, partially cross-linked or preferably linear.

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- any organosilicone of formula H-SXC where SXC is any such group hereinafter defined, and derivatives thereof.

-reactive silicones and phenyl silicones

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The choice of molecular weight of the silicones is mainly determined by processability factors. However, the molecular weight of silicones is usually indicated by reference to the viscosity of the material. Preferably, the silicones are liquid and typically have a viscosity in the range 20 mPas to 300,000 mPas. Suitable silicones include dimethyl,  
10 methyl (aminoethylaminoisobutyl) siloxane, typically having a viscosity of from 100 mPas to 200 mPas with an average amine content of ca. 2mol% and, for example, Rhodorsil Oil 21645, Rhodorsil Oil Extrasoft and Wacker Finish 1300. These viscosities are typically measured at  $21\text{ s}^{-1}$ , as are other viscosities referred to herein, unless specifically indicated to the contrary.

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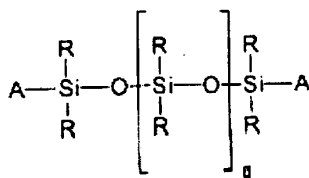
In general, however, it is preferred to use a silicone oil or mixture of silicone oils with a low viscosity, eg in the range of from 200 to 5,500 mPas, for example from 200 to 5,000 mPas. This makes the silicone easier to emulsify and also facilitates penetration of the silicone part of the substituted polysaccharide to penetrate into the silicone  
20 droplets in the emulsion.

For example, where a silicone has a viscosity above 5,000 mPas or above 5,500 mPas, it is preferred to incorporate some of a more volatile or low viscosity silicone, such as DC245 ex Dow Corning. This volatile or low viscosity silicone does not have to  
25 be one which endows a softening benefit. A typical result of such incorporation is as follows.

<u>Commercial Silicone Wt%</u>	<u>DC245</u>	<u>Viscosity mPas</u>
100	0	6,127
91	9	4,176
80	20	2,726
66	34	1,181
50	50	502
34	66	223

The amount of low viscosity/volatile silicone, especially a non-softening silicone, is preferably from 5% to 40%, more preferably from 10% to 30% by weight of the total silicone.

- 5 More specifically, materials such as polyalkyl or polyaryl silicones with the following structure can be used :



- 10 The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicones remain fluid at room temperature.

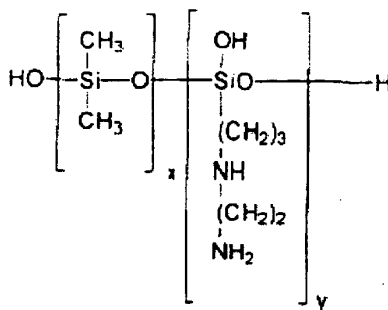
- R preferably represents a phenyl, a hydroxy, an alkyl or an aryl group. The two R groups on the silicone atom can represent the same group or different groups. More preferably, the two R groups represent the same group preferably, a methyl, an ethyl, a propyl, a phenyl or a hydroxy group. "q" is preferably an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. Suitable A groups include hydrogen, methyl, methoxy, ethoxy, hydroxy, propoxy, and aryloxy.

- 20 Preferred alkylsiloxanes include polydimethyl siloxanes having a viscosity of greater than about 10,000 centistokes (cst) at 25°C; and a most preferred silicone is a reactive silicone, i.e. where A is an OH group.

- Suitable methods for preparing these silicone materials are disclosed in US-A-2,826,551 and US-A-3,964,500.

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Other useful silicone materials include materials of the formula:



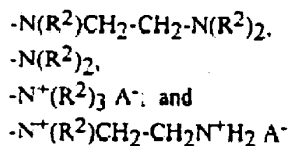
wherein x and y are integers which depend on the molecular weight of the silicone, the viscosity being from about 10,000 (cst) to about 500,000 (cst) at 25°C. This material is also known as "amodimethicone".

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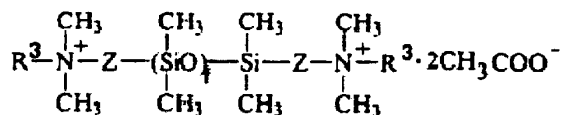
Other silicone materials which can be used, correspond to the formulae:



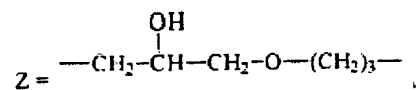
- wherein G is selected from the group consisting of hydrogen, phenyl, OH, and/or C<sub>1-8</sub> alkyl; a denotes 0 or an integer from 1 to 3; b denotes 0 or 1; the sum of n + m is a number from 1 to about 2,000; R<sup>1</sup> is a monovalent radical of formula CpH<sub>2p</sub>L in which p is an integer from 2 to 8 and L is selected from the group consisting of



- wherein each R<sup>2</sup> is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, and each A<sup>-</sup> denotes a compatible anion, e.g. a halide ion; and



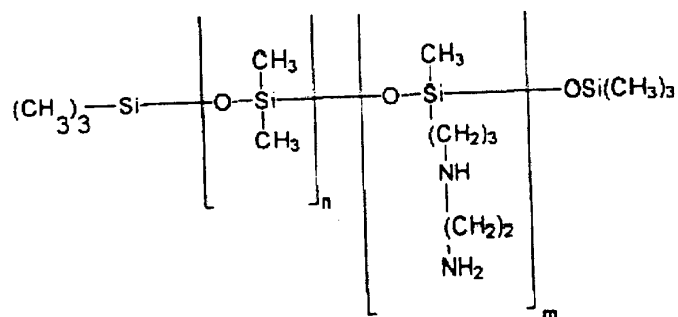
wherein



$R^3$  denotes a long chain alkyl group; and  $f$  denotes an integer of at least about 2.

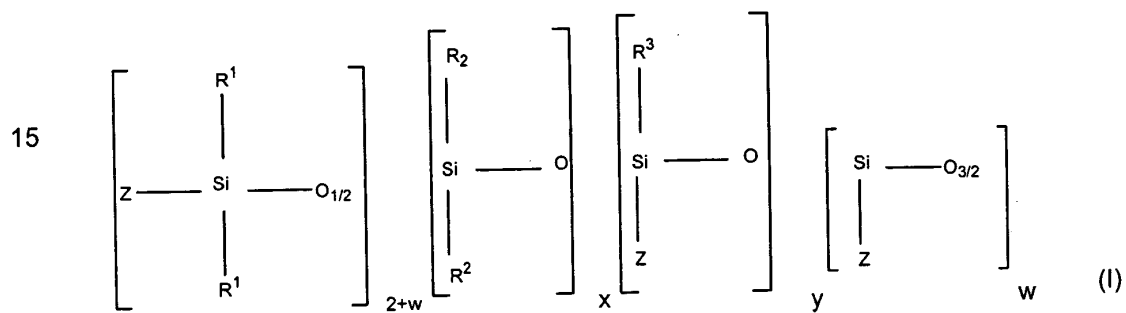
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Another silicone material which can be used, has the formula:



wherein  $n$  and  $m$  are the same as before.

- 10 Other suitable silicones comprise linear, cyclic, or three-dimensional polyorganosiloxanes of formula (I)



wherein

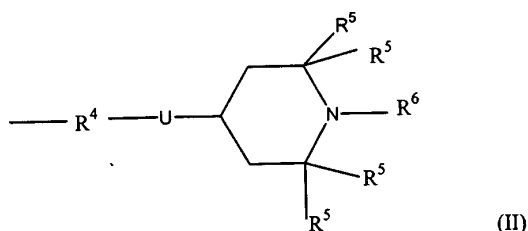
(1) the symbols  $Z$  are identical or different, represent  $R^1$ , and/or  $V$ ;

(2)  $R^1$ ,  $R^2$  and  $R^3$  are identical or different and represent a monovalent hydrocarbon radical chosen from the linear or branched alkyl radicals having 1 to 4 carbon atoms, the linear or branched alkoxy radicals having 1 to 4 carbon atoms, a phenyl radical, preferably a hydroxy radical, an ethoxy radical, a methoxy radical or a methyl radical;

5 and

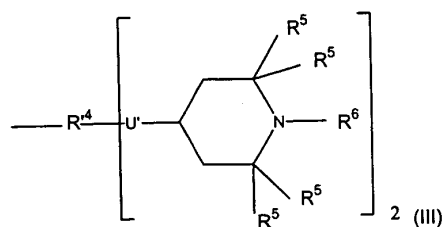
(3) the symbols V represent a group of sterically hindered piperidinyl functions chosen from

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or

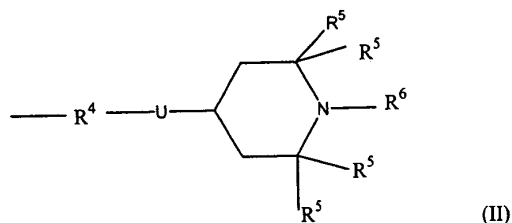
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For the groups of formula II

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-  $R^4$  is a divalent hydrocarbon radical chosen from

- linear or branched alkylene radical, having 2 to 18 carbon atoms;
- linear or branched alkylene-carbonyl radical where the alkylene part is linear or branched, comprising 2 to 20 carbon atoms;



- linear or branched alkylene-cyclohexylene where the alkylene part is linear or branched, comprising 2 to 12 carbon atoms and the cyclohexylene comprises an OH group and possibly 1 or 2 alkyl radicals having 1 to 4 carbon atoms;

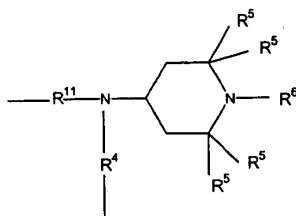
5 - the radicals of the formula  $-R^7-O-R^7$  where the  $R^7$  radical is identical or different represents an alkylene radical having 1 to 12 carbon atoms;

- the radicals of the formula  $-R^7-O-R^7$  where the  $R^7$  radical is as indicated previously and one or both are substituted by one or two OH groups;

- the radicals of the formula  $-R^7-COO-R^7$  where the  $-R^7$  radicals are as indicated previously;

10 - the radicals of formula  $R^8-O-R^9-O-CO-R^8$  where the  $R^8$  and  $R^9$  radicals are identical or different, represent alkylene radicals and have 2 to 12 carbon atoms and the radical  $R^9$  is possibly substituted with a hydroxyl radical;

15 - U represents  $-O-$  or  $-NR^{10}-$ ,  $R^{10}$  is a radical chosen from a hydrogen atom, a linear or branched alkyl radical comprising 1 to 6 carbon atoms and a divalent radical of the formula:



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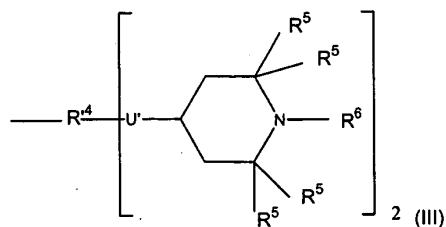
where  $R^4$  is as indicated previously,  $R^5$  and  $R^6$  have the meaning indicated below et  $R^{11}$  represents a divalent alkylene radical, linear or branched, having 1 to 12 carbon atoms, one of the valent bonds (one of  $R^{11}$ ) is connected to an atom of  $-NR^{10}-$ , the other (one of  $R^4$ ) is connected to a silicone atom;

25 -the radical  $R^5$  is identical or different, chosen from the linear or branched alkyl radicals having 1 to 3 carbon atoms and the phenyl radical;

-the radical  $R^6$  represents a hydrogen radical or the  $R^5$  radical or O.

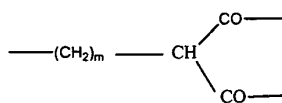
For the groups of formula (III):

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$\text{R}^4$  is chosen from a trivalent radical of the formula:

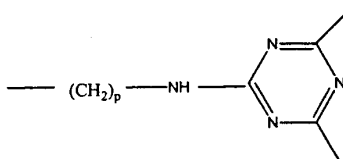


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where  $m$  represents a number between 2 and 20,

and a trivalent radical of the formula:

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where  $p$  represents a number between 2 and 20;

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- U represents  $\text{---O---}$  or  $\text{NR}^{12}$ ,  $\text{R}^{12}$  is a radical chosen from a hydrogen atom, a linear or branched alkyl radical comprising 1 to 6 carbon atoms;
- $\text{R}^5$  and  $\text{R}^6$  have the same meaning as proposed for formula (II); and

30 (4)

- the number of units  $\text{---Si---}$  without group V comprises between 10 and 450
- the number of units  $\text{---Si---}$  with group V comprises between 1 and 5,
- $0 \leq w \leq 10$  and  $8 \leq y \leq 448$ .

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### THE PERFUME COMPONENT

Perfumes, especially those used in laundry treatment products consist of at least one but usually, a mixture of a plurality of fragrances of natural and/or synthetic origin  
5 dispersed, or more usually dissolved in a vehicle or carrier. The vehicle or carrier may be aqueous (i.e. water or water plus one or more water-miscible solvents) or it may consist solely of one or more organic solvents which may or may not be water-miscible, even though water is substantially absent.

10 In the case of the present invention, a perfume component comprising one or more fragrances must be dispersed or dissolved in the silicone. Preferably, it is dissolved. Optionally, a further perfume component comprising one or more other fragrances may be not soluble or dispersible in the silicone, although that is less preferred. It is also preferred for the vehicle or carrier to be dissolved or dispersed in the silicone.

15 The dissolved and/or dispersed perfume component is preferably present in a weight ratio of from 1:10,000 to 1:5, preferably from 1:1,000 to 1:10 relative to the silicone. Where all or part of the carrier or vehicle and the dissolved or dispersed perfume component of the perfume are dissolved or dispersed in the silicone, the weight ratio of  
20 the total of all dissolved and dispersed parts of the perfume to the amount of the silicone is preferably from 1:1,000 to 2:1, more preferably from 1:100 to 1:5, especially from 1:50 to 1:10.

### Perfume Processing

25 The perfume may be admixed with all or part of the silicone prior to incorporation in the composition as a whole (whether that composition is a component of a laundry treatment composition *per se*). The step of admixture may be carried out in any suitable apparatus such as a high shear mixer. The amount of perfume is preferably  
30 incorporated in a weight ratio to the final silicone content of the composition of from 1:1,000 to 2:1, more preferably from 1:100 to 1:5, especially from 1:50 to 1:10.

### COMPOSITIONS

The compositions of the invention comprising the silicone and at least the dispersed or dissolved perfume component may themselves be incorporated in a composition which is a laundry treatment composition. The term "laundry treatment composition" is intended to refer to a composition as sold to, and dosed by the consumer e.g. in the wash or rinse. However, compositions of the invention may also constitute a component for a laundry treatment composition. A composition which is a component for a laundry treatment composition is one which is incorporated in the laundry treatment composition during manufacture of the latter.

#### 10 Components for Laundry Treatment Compositions

Compositions consisting only of, or mainly of (e.g. up to 95% by weight of that composition) the silicone and dissolved or dispersed perfume component and optionally also, perfume vehicle and carrier, may be incorporated in a laundry treatment composition. However, generally these compositions also comprise a deposition aid for the silicone and the dissolved or dispersed perfume component. Alternatively, or additionally, such a deposition aid may be separately incorporated in the laundry treatment composition.

20 A preferred deposition aid comprises a polymeric material comprising one or more moieties for enhancing affinity for a fabric, especially for cotton or a cotton-containing fabric and one or more silicone moieties.

Preferably, the deposition aid is not a cationic deposition aid. It is especially preferred that the deposition aid is not a cationic guar gum derivative such as guar hydroxypropyltrimmonium chloride. In particular, it is preferred that the deposition aid is not Jaguar C13S.

One preferred class of deposition aids are substituted polysaccharides. These are described further hereinbelow.

#### Emulsions

The silicone with dispersed or dissolved perfume component and deposition aid can be provided in the form of an emulsion for use in laundry treatment compositions.

One preferred emulsion according to the invention comprises a silicone comprising a dispersed or dissolved perfume component and a substituted polysaccharide comprising  $\beta_{1-4}$  linkages having covalently bonded on the polysaccharide moiety thereof, at least one deposition enhancing group which undergoes a chemical change in water at a use temperature to increase the affinity of the substituted polysaccharide to a substrate, the substituted polysaccharide further comprising one or more independently selected silicone chains.

10 The emulsion must contain another liquid component as well as the silicone with dispersed or dissolved silicone component, preferably a polar solvent, such as water. The emulsion has typically 30 to 99.9%, preferably 40 to 99% of the other liquid component (eg water). Low water emulsions may be for example 30 to 60% water, preferably 40 to 55% water. High water emulsions may be for example 60 to 99.9% water, preferably 80 to 99% water. Moderate water emulsions may be for example 55 to 80% water.

The emulsion may contain an emulsifying agent, preferably an emulsifying surfactant for the silicone with dispersed or dissolved perfume component and polysaccharide.

20 The emulsifying agent is especially one or more surfactants, for example, selected from any class, sub class or specific surfactant(s) disclosed herein in any context. The emulsifying agent most preferably comprises or consists of a non-ionic surfactant. Additionally or alternatively, one or more selected additional surfactants from anionic, cationic, zwitterionic and amphoteric surfactants may be incorporated in or used as the emulsifying agent.

Suitable non-ionic surfactants include the (poly)alkoxylated analogues of saturated or unsaturated fatty alcohols, for example, having from 8 to 22, preferably from 9 to 18, more preferably from 10 to 15 carbon atoms on average in the hydrocarbon chain thereof and preferably on average from 3 to 11, more preferably from 4 to 9 alkyleneoxy groups. Most preferably, the alkyleneoxy groups are independently selected from ethyleneoxy, propyleneoxy and butyleneoxy, especially ethyleneoxy and propyleneoxy, or solely ethyleneoxy groups and alkyl polyglucosides as disclosed in EP 0 495 176.

Preferably, the (poly)alkoxylated analogues of saturated or unsaturated fatty alcohols, have a hydrophilic-lipophilic balance (HLB) of between 8 to 18. The HLB of a polyethoxylated primary alcohol nonionic surfactant can be calculated by

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$$\text{HLB} = \frac{\text{MW (EO)}}{\text{MW(TOT)} \times 5} \times 100$$

10 where

MW (EO) = the molecular weight of the hydrophilic part (based on the average number of EO groups)

15 MW(TOT) = the molecular weight of the whole surfactant (based on the average chain length of the hydrocarbon chain)

This is the classical HLB calculation according to Griffin (J. Soc. Cosmentic Chemists, 5 (1954) 249-256).

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For analogous nonionics with a mix of ethyleneoxy (EO), propyleneoxy (PO) and/or butyleneoxy (BO) hydrophilic groups, the following formula can be used;

$$\text{HLB} = \frac{\text{MW(EO)} + 0.57 \text{ MW(PO)} + 0.4 \text{ MW (BO)}}{\text{MW (TOT)} \times 5}$$

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Preferably, the alkyl polyglucosides may have the following formula;



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in which R is a linear or branched, saturated or unsaturated aliphatic alkyl radical having 8 to 18 carbon atoms or mixtures thereof, and Z<sub>n</sub> is a polyglycosyl radical with n=1.0 to 1.4 hexose or pentose units or mixtures. Preferred examples of alkylpolyglucosides include Glucopon™.

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- Whether in a composition of a component (especially an emulsion) to be incorporated in a laundry treatment composition or in a laundry treatment composition as a whole, the weight ratio of silicone to the deposition aid is preferably from 1:1 to 100:1, more preferably from 5:1 to 20:1. The weight ratio of deposition aid to emulsifying agent is from 1:2 to 100:1, preferably 2:1 to 10:1. Further, in any such composition (especially emulsion components) the weight ratio of silicone with dissolved or dispersed perfume component to emulsifying agent is from 100:1 to 2:1, preferably from 100:3 to 5:1, more preferably from 15:1 to 7:1.
- 10 Preferably, the total amount of silicone with dissolved or dispersed perfume component is from 50 to 95%, preferably from 60 to 90%, more preferably from 70 to 85% by weight of the silicone with dissolved or dispersed perfume component plus deposition aid plus any emulsifying agent.

15 Emulsion Processing

- When in the form of an emulsion, the emulsion is prepared by mixing the silicone with dissolved or dispersed perfume component deposition aid, other liquid component, e.g. water and preferably, also an emulsifying agent, such as a surfactant, especially a non-ionic surfactant, e.g. in a high shear mixer.
- 20

- Whether or not pre-emulsified, the silicone with dissolved or dispersed perfume component and the deposition aid may be incorporated by admixture with other components of a laundry treatment composition. Preferably, the emulsion is present at a level of from 0.0001 to 40%, more preferably from 0.001 to 30%, even more preferably from 0.1 to 20%, especially from 1 to 15% and for example from 5 to 10% by weight of the total composition.
- 25

- When the silicone with dissolved or dispersed perfume component is to be incorporated in an emulsion such as hereinbefore described, the admixture of perfume are all or part of the silicone is preferably carried out as a processing step before, especially immediately before formation of the emulsion.
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Substituted Polysaccharides

A preferred deposition aid, whether a laundry treatment composition or a component therefore, is a substituted polysaccharide.

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The substituted polysaccharide is preferably water-soluble or water-dispersible in nature and comprises a polysaccharide substituted with at least one silicone moiety attached to the polysaccharide aid by a hydrolytically stable bond.

- 10 In such a substituted polysaccharide, the silicone chain is preferably attached to the polysaccharide by a covalent stable bond. That means that the bonding of the silicone should be sufficiently stable so as not to undergo hydrolysis in the environment of the treatment process for the duration of that process. For example, in laundry cleaning applications, the substituted polysaccharide should be sufficiently stable so that the
- 15 bond between the silicone and polysaccharide does not undergo hydrolysis in the wash liquor, at the wash temperature, before the silicone has been deposited onto the fabric.

- Preferably, the bond between the silicone and the polysaccharide is such that the decay rate constant ( $k_d$ ) of the material in an aqueous solution at 0.01 wt% of the
- 20 material together with 0.1 wt% of anionic surfactant at a temperature of 40°C at a pH of 10.5 is such that  $k_d < 10^{-3} \text{s}^{-1}$ .

By water-soluble, as used herein, what is meant is that the material forms an isotropic solution on addition to water or another aqueous solution.

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By water-dispersible, as used herein, what is meant is that the material forms a finely divided suspension on addition to water or another aqueous solution.

- By an increase in the affinity of the substituted polysaccharide for a substrate such as a
- 30 textile fabric upon a chemical change, what is meant is that at some time during the treatment process, the amount of material that has been deposited is greater when the chemical change is occurring or has occurred, compared to when the chemical change has not occurred and is not occurring, or is occurring more slowly, the comparison being made with all conditions being equal except for that change in the conditions
- 35 which is necessary to affect the rate of chemical change.



Deposition onto a substrate includes deposition by adsorption, co-crystallisation, entrapment and/or adhesion.

5    The Polysaccharide Part

The polysaccharide is preferably  $\beta_{1,4}$  linked and is a cellulose, a cellulose derivative, or another  $\beta_{1,4}$ -linked polysaccharide having an affinity for cellulose, such as mannan and glucomannan.

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Preferably, the polysaccharide has only  $\beta_{1,4}$  linkages. Optionally, the polysaccharide has linkages in addition to the  $\beta_{1,4}$  linkages, such as  $\beta_{1,3}$  linkages. Thus, optionally some other linkages are present. Polysaccharide backbones which include some material which is not a saccharide ring are also within the ambit of the present invention (whether terminal or within the polysaccharide chain).

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The polysaccharide may be straight or branched. Many naturally occurring polysaccharides have at least some degree of branching, or at any rate at least some saccharide rings are in the form of pendant side groups (which are therefore not in themselves counted in determining the degree of substitution) on a main polysaccharide backbone.

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A polysaccharide comprises a plurality of saccharide rings which have pendant hydroxyl groups. In the substituted polysaccharides of the present invention, at least some of these hydroxyl groups are independently substituted by, or replaced with, one or more other substituents, at least one being a silicone chain. The "average degree of substitution" for a given class of substituent means the average number of substituents of that class per saccharide ring for the totality of polysaccharide molecules in the sample and is determined for all saccharide rings.

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The Deposition Enhancing Group(s)

A deposition enhancing group is a group which undergoes a chemical change in use, and is attached to the polysaccharide agent group by means of a covalent stable bond.

This chemical change results in an increase of the affinity of the material for the substrate and is referred to further below.

- 5 The chemical change which causes the increased substrate affinity is preferably caused by hydrolysis, perhydrolysis or bond-cleavage, optionally catalysed by an enzyme or another catalyst. Hydrolysis of substituent ester-linked groups is typical.

- 10 By ester linkage is meant that the hydrogen of an -OH group has been replaced by a substituent such as R'-CO-, R'SO<sub>2</sub>- etc to form a carboxylic acid ester, sulphonic acid ester (as appropriate) etc together with the remnant oxygen attached to the saccharide ring. In some cases, the group R' may for example contain a heteroatom, e.g. as an -NH- group attached to the carbonyl, sulphonyl etc group, so that the linkage as a whole could be regarded as a urethane etc linkage. However, the term ester linkage is still to be construed as encompassing these structures.

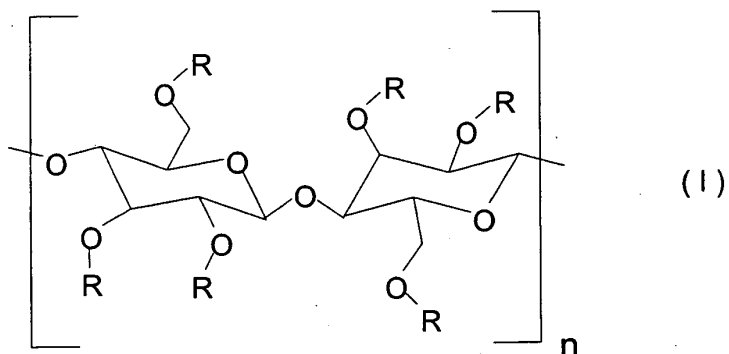
- 15 The average degree of substitution of these pendant groups which undergo the chemical change is preferably from 0.1 to 3 (e.g. from 0.3 to 3), more preferably from 0.1 to 1 (e.g. from 0.3 to 1)

## 20 The Silicone Chain(s)

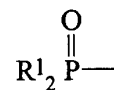
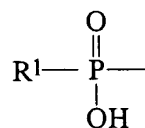
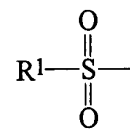
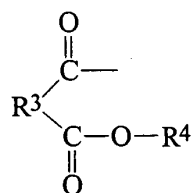
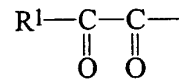
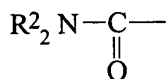
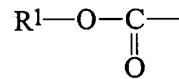
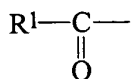
- As used herein the term "silicone chain" means a polysiloxane or derivative thereof. In the section "Preferred Overall Structure" hereinbelow, various preferred silicone chains are recited and these are typically suitable, whether or not the substituted  
25 polysaccharide conforms to the preferred overall structure,

### Preferred Overall Structures

- Preferred substituted polysaccharides of the invention are cellulosic polymers of  
30 formula (I):-



- (optional  $\beta_{1,3}$  and/or other linkages and/or other groups being permitted in the above formula (I)) wherein at least one or more -OR groups of the polymer are substituted by
- 5 or replaced by independently selected silicone chains and at least one or more R groups are independently selected from groups of formulae:-



- 10
- 15 wherein each  $\text{R}^1$  is independently selected from  $\text{C}_{1-20}$  (preferably  $\text{C}_{1-6}$ ) alkyl,  $\text{C}_{2-20}$  (preferably  $\text{C}_{2-6}$ ) alkenyl (e.g. vinyl) and  $\text{C}_{5-7}$  aryl (e.g. phenyl) any of which is optionally substituted by one or more substituents independently selected from  $\text{C}_{1-4}$  alkyl,  $\text{C}_{1-12}$  (preferably  $\text{C}_{1-4}$ ) alkoxy, hydroxyl, vinyl and phenyl groups;

each  $R^2$  is independently selected from hydrogen and groups  $R^1$  as hereinbefore defined;

- 5  $R^3$  is a bond or is selected from  $C_{1-4}$  alkylene,  $C_{2-4}$  alkenylene and  $C_{5-7}$  arylene (e.g. phenylene) groups, the carbon atoms in any of these being optionally substituted by one or more substituents independently selected from  $C_{1-12}$  (preferably  $C_{1-4}$ ) alkoxy, vinyl, hydroxyl, halo and amine groups;
- 10 each  $R^4$  is independently selected from hydrogen, counter cations such as alkali metal (preferably Na) or  $\frac{1}{2}$  Ca or  $\frac{1}{2}$  Mg, and groups  $R^1$  as hereinbefore defined; and

- groups R which together with the oxygen atom forming the linkage to the respective saccharide ring forms an ester or hemi-ester group of a tricarboxylic- or higher
- 15 polycarboxylic- or other complex acid such as citric acid, an amino acid, a synthetic amino acid analogue or a protein;

any remaining R groups being selected from hydrogen and other substituents.

- 20 For the avoidance of doubt, as already mentioned, in formula (I), some of the R groups may optionally have one or more structures, for example as hereinbefore described. For example, one or more R groups may simply be hydrogen or an alkyl group.

- Preferred groups which undergo the chemical change may for example be
- 25 independently selected from one or more of acetate, propanoate, trifluoroacetate, 2-(2-hydroxy-1-oxopropoxy) propanoate, lactate, glycolate, pyruvate, crotonate, isovalerate, cinnamate, formate, salicylate, carbamate, methylcarbamate, benzoate, gluconate, methanesulphonate, toluene, sulphonate, groups and hemiester groups of fumaric, malonic, itaconic, oxalic, maleic, succinic, tartaric, aspartic, glutamic, and malic acids.

- 30 Particularly preferred such groups are the monoacetate, hemisuccinate, and 2-(2-hydroxy-1-oxopropoxy)propanoate. The term "monoacetate" is used herein to denote those acetates with the degree of substitution of 1 or less on a cellulose or other  $\beta$ -1,4 polysaccharide backbone.

Cellulose esters of hydroxyacids can be obtained using the acid anhydride in acetic acid solution at 20–30°C and in any case below 50°C. When the product has dissolved the liquid is poured into water (b.p. 316,160). Tri-esters can be converted to secondary products as with the triacetate. Glycollic and lactic ester are most common.

Cellulose glycollate may also be obtained from cellulose chloracetate (GB-A-320 842) by treating 100 parts with 32 parts of NaOH in alcohol added in small portions.

- 10 An alternative method of preparing cellulose esters consists in the partial displacement of the acid radical in a cellulose ester by treatment with another acid of higher ionisation constant (FR-A-702 116). The ester is heated at about 100°C with the acid which, preferably, should be a solvent for the ester. By this means cellulose acetate-oxalate, tartrate, maleate, pyruvate, salicylate and phenylglycollate have been
- 15 obtained, and from cellulose tribenzoate a cellulose benzoate-pyruvate. A cellulose acetate-lactate or acetate-glycollate could be made in this way also. As an example cellulose acetate (10 g.) in dioxan (75 ml.) containing oxalic acid (10 g.) is heated at 100°C for 2 hours under reflux.
- 20 Multiple esters are prepared by variations of this process. A simple ester of cellulose, e.g. the acetate, is dissolved in a mixture of two (or three) organic acids, each of which has an ionisation constant greater than that of acetic acid ( $1.82 \times 10^{-5}$ ). With solid acids suitable solvents such as propionic acid, dioxan and ethylene dichloride are used. If a mixed cellulose ester is treated with an acid this should have an ionisation
- 25 constant greater than that of either of the acids already in combination.

- A cellulose acetate-lactate-pyruvate is prepared from cellulose acetate, 40 per cent. acetyl (100 g.), in a bath of 125 ml. pyruvic acid and 125 ml. of 85 per cent. lactic acid by heating at 100°C for 18 hours. The product is soluble in water and is precipitated
- 30 and washed with ether-acetone. M.p. 230-250°C.

In the case of those materials having a cellulose backbone and pendant ester groups, without being bound by any particular theory or explanation, the inventors have conjectured that the mechanism of deposition is as follows.

Cellulose is substantially insoluble in water. Attachment of the ester groups to make a cellulose derivative causes disruption of the hydrogen bonding between rings of the cellulose chain or chains, thus increasing water solubility or dispersibility. In the treatment liquor, the ester groups are hydrolysed, causing the cellulose derivative to increase its affinity for the substrate, e.g. the fabric.

In the case when solubilising groups are attached to the polysaccharide, this is typically via covalent bonding and, may be pendant upon the backbone or incorporated therein. The type of solubilising group may alter according to where the group is positioned with respect to the backbone.

In this specification the "n" subscript used in the general formulae of the substituted polysaccharide is a generic reference to a polymer. Although "n" can also mean the actual (average) number of repeat units present in the polysaccharide, it is more meaningful to refer to "n" by the number average molecular weight.

The number average molecular weight ( $M_n$ ) of the substituted polysaccharide part may typically be in the range of 1,000 to 200,000, for example 2,000 to 100,000, e.g. as measured using GPC with multiple angle laser scattering detection.

20

The silicone chains preferred for use to substitute or replace (dependent upon the synthetic route use to prepare the substituted polysaccharides of the invention) at least one -OR group in the compounds of formula (I) are representative of preferred silicone chains for use in substituted polysaccharides used in the invention as a whole, i.e. whether or not the overall structure conforms to formula (I).

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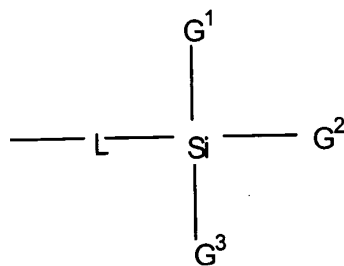
Preferably, the average degree of substitution for the silicone chains is from 0.001 to 0.5, preferably from 0.01 to 0.5, more preferably from 0.01 to 0.1, still more preferably from 0.01 to 0.05.

30

Even more preferably the average degree of substitution for the silicone chains is from 0.00001 to 0.1, more preferably from 0.001 to 0.04, even more preferably from 0.001 to 0.01.

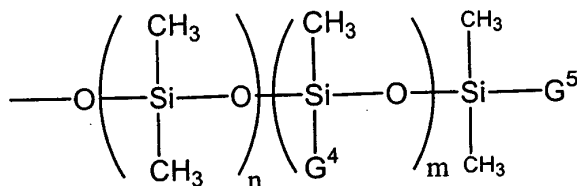
35 Preferred silicone chains suitable for this use are those of formula:

5



wherein L is absent or is a linking group and one or two of substituents  $\text{G}^1$ - $\text{G}^3$  is a  
 10 methyl group, the remainder being selected from groups of formula

15



the  $\text{--- Si(CH}_3)_2\text{O---}$  groups and the  $\text{--- Si(CH}_3)_0(\text{G}^4)\text{---}$  groups being arranged in random or  
 20 block fashion, but preferably random.

wherein n is from 5 to 1000, preferably from 10 to 200 and m is from 0 to 100,  
 preferably from 0 to 20, for example from 1 to 20.

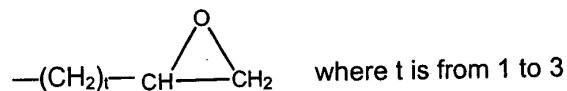
25  $\text{G}^4$  is selected from groups of formula:

$\text{---(CH}_2)_p\text{---CH}_3$ , where p is from 1 to 18

$\text{---(CH}_2)_q\text{---NH---(CH}_2)_r\text{---NH}_2$  where q and r are independently from 1 to 3

$\text{---(CH}_2)_s\text{---NH}_2$ , where s is from 1 to 3

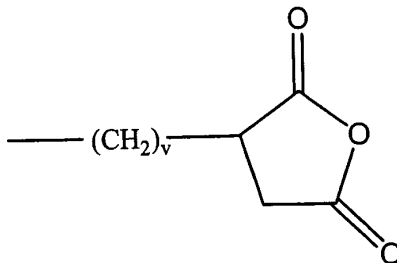
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35

—(CH<sub>2</sub>)<sub>u</sub>—COOH, where u is from 1 to 10,

5



10

where v is from 1 to 10, and

—(CH<sub>2</sub> CH<sub>2</sub>O)<sub>w</sub>—(CH<sub>2</sub>)<sub>x</sub> H, where w is from 1 to 150, preferably from 10 to 20 and x is from 0 to 10;

15

and G<sup>5</sup> is independently selected from hydrogen, groups defined above for G<sup>4</sup>, —OH, —CH<sub>3</sub> and —C(CH<sub>3</sub>)<sub>3</sub>.

#### Other Substituents

20

As well as the silicone chain(s) and the pendant group(s) which undergo a chemical change to enhance deposition, pendant groups of other types may optionally be present, i.e. groups which do not confer a benefit and which do not undergo a chemical change to enhance substrate affinity. Within that class of other groups is the sub-class of groups for enhancing the solubility of the material (e.g. groups which are, or contain one or more free carboxylic acid/salt and/or sulphonic acid/salt and/or sulphate groups).

25

Examples of solubility enhancing substituents include carboxyl, sulphonyl, hydroxyl, (poly)ethyleneoxy- and/or (poly)propyleneoxy-containing groups, as well as amine groups.

30

The other pendant groups preferably comprise from 0% to 65%, more preferably from 0% to 10% of the total number of pendant groups. The water-solubilising groups could comprise from 0% to 100% of those other groups but preferably from 0% to 20%, more

35



preferably from 0% to 10%, still more preferably from 0% to 5% of the total number of other pendant groups.

#### Synthetic Routes

5

As described above, preferred substituted polysaccharides of the present invention are those of formula (I). Further, preferred silicone chains, whether for the compounds of formula (I) or any other substituted polysaccharides of the invention are preferably attached via a linking group "-L-". This linking group is the residue of the reactants used to form the substituted polysaccharide.

10

The substituted polysaccharides of the invention can be made thus:

- (a) a polysaccharide is first substituted with one or more deposition enhancing groups; and
- (b) one or more silicone groups are then attached.

15

If any other substituents are to be present, these may already be present in the commercially available polysaccharide, or attached before or after step (a) and/or (b).

20

Whilst steps (a) and (b) can be reversed, the reaction whereby step (a) is conducted first is preferred.

The deposition enhancing group(s) is/or are attached in step (a) according to the methodology described in WO-A-00/18861.

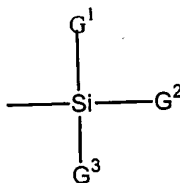
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In step (b), one or more hydroxyl groups on the polysaccharide are reacted with a reactive group attached to the silicone chain, or the hydroxyl group(s) in question is/are converted to another group capable of reaction with a reactive group attached to the silicone chain. Listed below, are suitable mutually reactive groups. In the case of hydroxyl groups, these may be the original hydroxyl group of the polysaccharide. However, either of a pair of these mutually reactive groups may be present on the polysaccharide and the other attached to the silicone chain, or *vice versa*, the reaction chemistry being chosen appropriately. In the following description, for convenience,

30

"PSC" refers to the polysaccharide chain with or without deposition enhancing group(s) and/or other substituent(s) already attached. "SXC" refers to the group

5

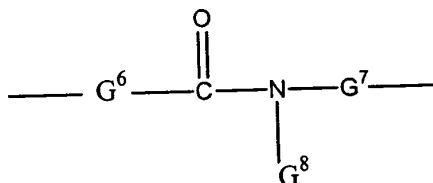


as hereinbefore defined.

- 10 Preferred linking groups —L— are selected from the following, wherein preferably, the left hand end of the group depicted is connected to the saccharide ring either direct or via the residual oxygen of one of the original saccharide —OH groups and the right hand end is connected to the moiety —Si(G<sup>1</sup>G<sup>2</sup>G<sup>3</sup>). Thus, the configuration as written is PSC-L-SXC. However, the reverse configuration SXC-L-PSC is also within the ambit
- 15 of this definition and this is also mentioned where appropriate.

Preferred linking groups -L- are selected from amide, ester, ether, urethane, triazine, carbonate, amine and ester-alkylene linkages.

- 20 A preferred amide linkage is:

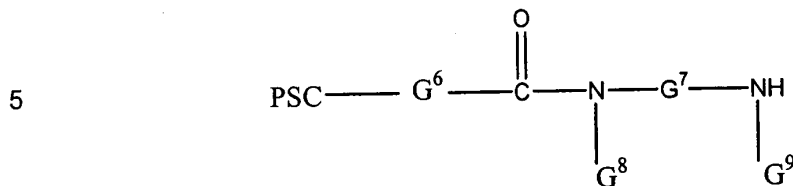


25

where G<sup>6</sup> and G<sup>7</sup> are each optionally present and are independently selected spacer groups, e.g. selected from C<sub>1-14</sub> alkylene groups, arylene, C<sub>1-4</sub> alkoxy, a residue of an oligo- or poly-ethylene oxide moiety, C<sub>1-4</sub> alkylamine or a polyamine groups and

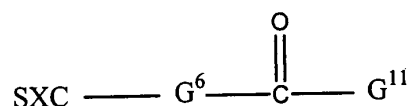
- 30 G<sup>8</sup> is hydrogen or C<sub>1-4</sub> alkyl.

This linkage can be formed by reacting



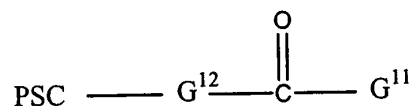
wherein  $\text{G}^7$  and  $\text{G}^8$  are as hereinbefore defined and  $\text{G}^9$  is hydrogen or  $\text{C}_{1-4}$  alkyl;

10 with a compound of formula:

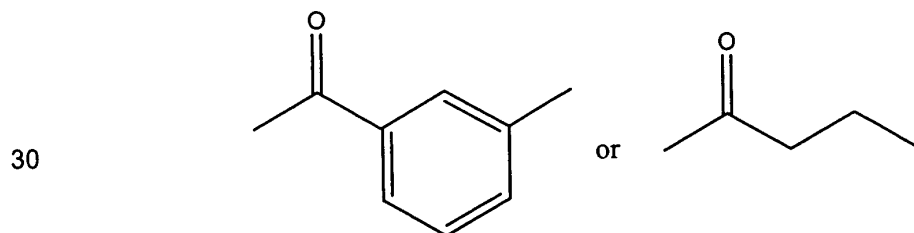


15 wherein  $\text{G}^{11}$  is hydroxy, a group with active ester functionality halo, or a leaving group suitable for nucleophilic displacement such as imidazole or an imidazole-containing group and wherein  $\text{G}^6$  is hereinbefore defined above, or  $-\text{CO}-\text{G}^{11}$  is replaced by a cyclic acid anhydride. Active ester synthesis is described in M. Bodanszky, "The Peptides", Vol. 1, Academic Press Inc., 1975, pp105 ff.

20 The reverse configuration linkage may be formed by reacting

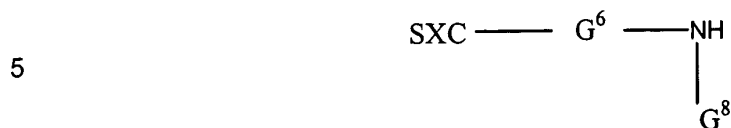


25 wherein  $\text{G}^{12}$  is a ring-opened carboxylic acid anhydride, phenylene, or a group of formula



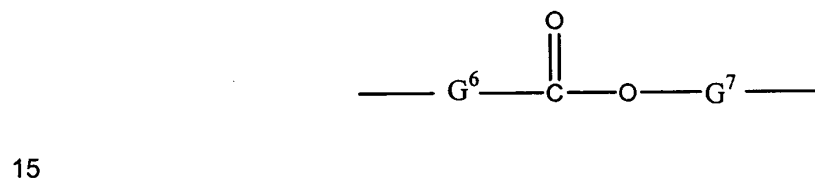
and  $G^{11}$  is as hereinbefore defined;

with the group of formula



where  $G^6$  and  $G^8$  are as hereinbefore defined.

10 A preferred ester linkage has the formula



wherein  $G^6$  and  $G^7$  are as hereinbefore defined,  $G^6$  optionally being absent.

This may be formed by reacting



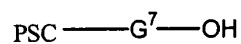
wherein  $G^{11}$  and  $G^{12}$  are as hereinbefore defined with



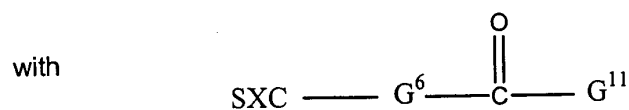
wherein  $G^6$  is as hereinbefore defined.

30

The reverse ester linkage formation may be formed by reacting



35 (i.e. the optionally modified polysaccharide with at least one residual —OH group)



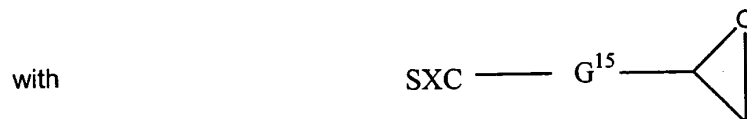
- 5 wherein  $\text{G}^6$  and  $\text{G}^{11}$  are as hereinbefore defined, or  $-\text{CO}-\text{G}^{11}$  may be replaced by a cyclic anhydride.

Preferred ether linkages have the formula



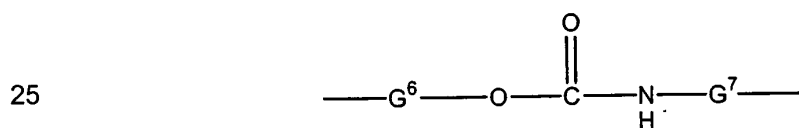
wherein  $\text{G}^6$  and  $\text{G}^7$  are as hereinbefore defined, optionally one being absent.

This linkage may be formed by reacting

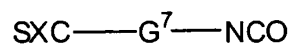
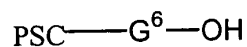


- 20 wherein  $\text{G}^{15}$  is  $\text{C}_{1-4}$  alkylene and  $\text{G}^6$  is optionally absent and is as hereinbefore defined.

A preferred urethane linkage is



- 30 wherein  $\text{G}^6$  and  $\text{G}^7$  are as hereinbefore defined,  $\text{G}^6$  optionally being absent (preferably absent in the configuration PSC-L-SXC)



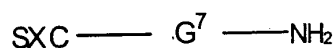
with

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wherein  $G^6$  and  $G^7$  are as hereinbefore defined,  $G^6$  optionally being absent (preferably absent in the configuration PSC-L-SXC)

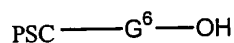
5 The reverse configuration is also possible but the simplest arrangement is PSC-L-SXC and wherein  $G^6$  is absent. Also most common is when  $G^7$  is alkylene.

The latter compound is made by reacting



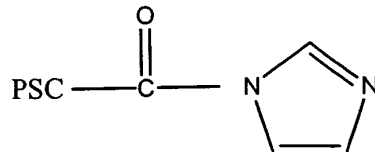
10 wherein  $G^7$  is as hereinbefore defined;  
with phosgene.

Another route is to react



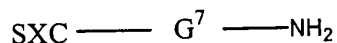
15

wherein  $G^6$  is as hereinbefore defined  
with carbonyl dimidazole to form



20

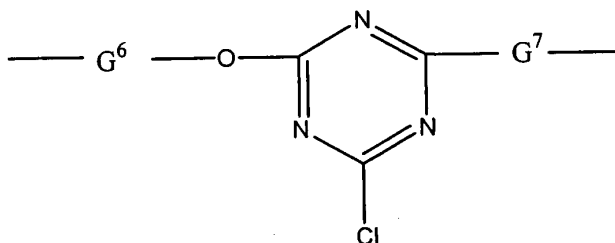
and react that product with



25

wherein  $G^7$  is as hereinbefore defined.

Preferred triazine linkages have the formula



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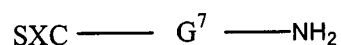
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wherein  $G^6$  and  $G^7$  are as hereinbefore defined,  $G^6$  optionally being absent.

These linkages may be formed by reacting

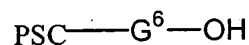


or



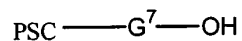
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wherein  $G^7$  is as hereinbefore defined with cyanuric chloride and then with

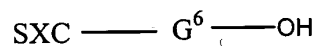


15 wherein  $G^6$  is as hereinbefore defined but may be absent;

or (reverse -L-) by reacting

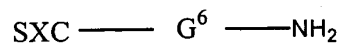


20 with cyanuric chloride (when  $G^7$  is as hereinbefore defined) and then with

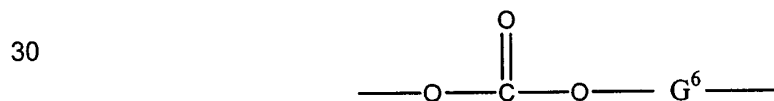


or

25



Preferred carbonate linkages have the formula



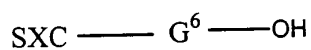
wherein  $G^6$  is as hereinbefore defined.

35

This linkage may be formed by reacting



with

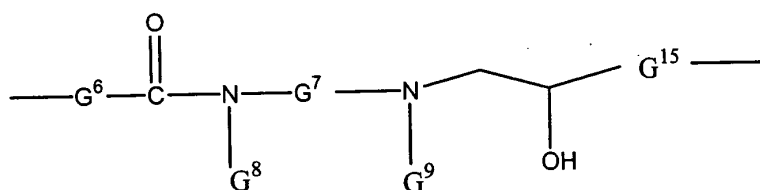


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in the presence of carbonyl dimidazole or phosgene

Preferred amine linkages have the formula

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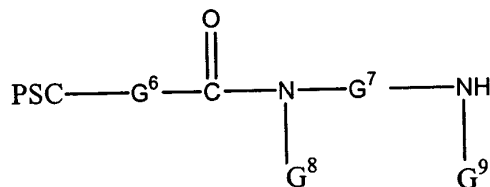


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wherein G<sup>6</sup>, G<sup>7</sup>, G<sup>8</sup>, G<sup>9</sup> and G<sup>15</sup> are as hereinbefore defined.

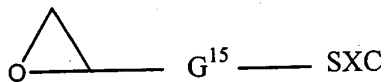
This linkage may be formed by reacting

20



wherein G<sup>6</sup>-G<sup>9</sup> are hereinbefore defined;

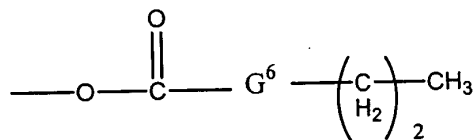
25 with



wherein G<sup>15</sup> is as hereinbefore defined.

Preferred ester-alkylene linkages have the formula

30



35

wherein G<sup>7</sup> is as hereinbefore defined.

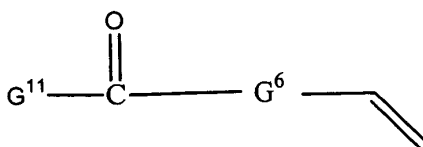


These linkages may be prepared by reacting



5

with



10

and then reacting with a hydrogen-terminated silicone chain compound (i.e.  $\text{G}^5 = \text{H}$ ) over a platinum catalyst.

#### Laundry Treatment Compositions

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The silicone with dissolved or dispersed perfume component and optionally also, any deposition aid, are incorporated together into laundry compositions, as separate ingredients or a composition which is an ingredient to be incorporated in the laundry treatment composition, especially as an emulsion. For example, such a composition may optionally also comprise only a diluent (which may comprise solid and/or liquid) and/or also it may comprise an active ingredient. Any deposition aid is typically included in said compositions at levels of from 0.001% to 10% by weight, preferably from 0.005% to 5%, most preferably from 0.01% to 3%.

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If the component is in the form of an emulsion, typical inclusion levels of the emulsion in the laundry treatment composition are from 0.0001 to 40%, more preferably from 0.001 to 30%, even more preferably from 0.1 to 20%, especially from 1 to 15% and for example from 5 to 10% by weight of the total composition.

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The active ingredient in the compositions is preferably a surface active agent or a fabric conditioning agent. More than one active ingredient may be included. For some applications a mixture of active ingredients may be used.

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The compositions of the invention may be in any physical form e.g. a solid such as a powder or granules, a tablet, a solid bar, a paste, gel or liquid, especially, an aqueous

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based liquid. In particular the compositions may be used in laundry compositions, especially in liquid, powder or tablet laundry composition.

The compositions of the present invention are preferably laundry compositions, especially main wash (fabric washing) compositions or rinse-added softening  
5 compositions. The main wash compositions may include a fabric softening agent and rinse-added fabric softening compositions may include surface-active compounds, particularly non-ionic surface-active compounds, if appropriate.

The detergent compositions of the invention may contain a surface-active compound  
10 (surfactant) which may be chosen from soap and non-soap anionic, cationic, non-ionic, amphoteric and zwitterionic surface-active compounds and mixtures thereof. Many suitable surface-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

15 The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and non-ionic compounds.

The compositions of the invention may contain linear alkylbenzene sulphonate,  
20 particularly linear alkylbenzene sulphonates having an alkyl chain length of C<sub>8</sub>-C<sub>15</sub>. It is preferred if the level of linear alkylbenzene sulphonate is from 0 wt% to 30 wt%, more preferably 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

The compositions of the invention may contain other anionic surfactants in amounts  
25 additional to the percentages quoted above. Suitable anionic surfactants are well-known to those skilled in the art. Examples include primary and secondary alkyl sulphates, particularly C<sub>8</sub>-C<sub>15</sub> primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulposuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

30 The compositions of the invention may also contain non-ionic surfactant. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C<sub>8</sub>-C<sub>20</sub> aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C<sub>10</sub>-C<sub>15</sub> primary

and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

- 5 It is preferred if the level of non-ionic surfactant is from 0 wt% to 30 wt%, preferably from 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

- 10 Any conventional fabric conditioning agent may be used in the compositions of the present invention. The conditioning agents may be cationic or non-ionic. If the fabric conditioning compound is to be employed in a main wash detergent composition the compound will typically be non-ionic. For use in the rinse phase, typically they will be cationic. They may for example be used in amounts from 0.5% to 35%, preferably from 1% to 30% more preferably from 3% to 25% by weight of the composition.

- 15 Suitable cationic fabric softening compounds are substantially water-insoluble quaternary ammonium materials comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C<sub>20</sub> or, more preferably, compounds comprising a polar head group and two alkyl or alkenyl chains having an average chain length greater than or equal to C<sub>14</sub>. Preferably the fabric softening compounds have
- 20 two long chain alkyl or alkenyl chains each having an average chain length greater than or equal to C<sub>16</sub>. Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C<sub>18</sub> or above. It is preferred if the long chain alkyl or alkenyl groups of the fabric softening compound are predominantly linear.

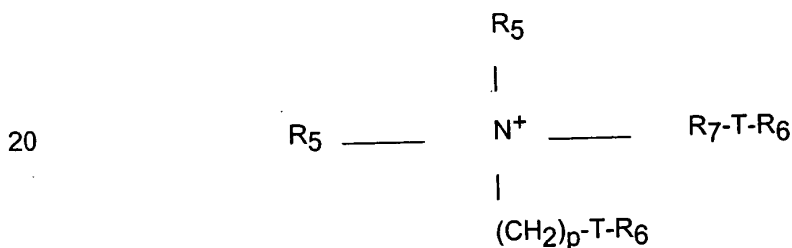
- 25 Quaternary ammonium compounds having two long-chain aliphatic groups, for example, distearyldimethyl ammonium chloride and di(hardened tallow alkyl) dimethyl ammonium chloride, are widely used in commercially available rinse conditioner compositions. Other examples of these cationic compounds are to be found in "Surfactants Science Series" volume 34 ed. Richmond 1990, volume 37 ed. Rubingh
- 30 1991 and volume 53 eds. Cross and Singer 1994, Marcel Dekker Inc. New York".

Any of the conventional types of such compounds may be used in the compositions of the present invention.

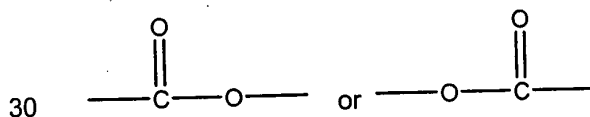
The fabric softening compounds are preferably compounds that provide excellent softening, and are characterised by a chain melting  $L_{\beta}$  to  $L_{\alpha}$  transition temperature greater than  $25^{\circ}\text{C}$ , preferably greater than  $35^{\circ}\text{C}$ , most preferably greater than  $45^{\circ}\text{C}$ . This  $L_{\beta}$  to  $L_{\alpha}$  transition can be measured by differential scanning calorimetry as defined in "Handbook of Lipid Bilayers", D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

Substantially water-insoluble fabric softening compounds are defined as fabric softening compounds having a solubility of less than  $1 \times 10^{-3}$  wt % in demineralised water at  $20^{\circ}\text{C}$ . Preferably the fabric softening compounds have a solubility of less than  $1 \times 10^{-4}$  wt%, more preferably less than  $1 \times 10^{-8}$  to  $1 \times 10^{-6}$  wt%.

Especially preferred are cationic fabric softening compounds that are water-insoluble quaternary ammonium materials having two  $\text{C}_{12-22}$  alkyl or alkenyl groups connected to the molecule via at least one ester link, preferably two ester links. An especially preferred ester-linked quaternary ammonium material can be represented by the formula:



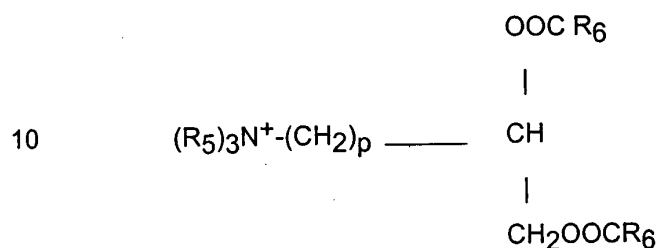
wherein each  $\text{R}_5$  group is independently selected from  $\text{C}_{1-4}$  alkyl or hydroxyalkyl groups or  $\text{C}_{2-4}$  alkenyl groups; each  $\text{R}_6$  group is independently selected from  $\text{C}_{8-28}$  alkyl or alkenyl groups; and wherein  $\text{R}_7$  is a linear or branched alkylene group of 1 to 5 carbon atoms, T is



and p is 0 or is an integer from 1 to 5.

Di(tallowoxyloxyethyl) dimethyl ammonium chloride and/or its hardened tallow analogue is an especially preferred compound of this formula.

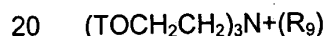
- 5 A second preferred type of quaternary ammonium material can be represented by the formula:



wherein R<sub>5</sub>, p and R<sub>6</sub> are as defined above.

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A third preferred type of quaternary ammonium material are those derived from triethanolamine (hereinafter referred to as 'TEA quats') as described in for example US 3915867 and represented by formula:



wherein T is H or (R<sub>8</sub>-CO-) where R<sub>8</sub> group is independently selected from C<sub>8-28</sub> alkyl or alkenyl groups and R<sub>9</sub> is C<sub>1-4</sub> alkyl or hydroxyalkyl groups or C<sub>2-4</sub> alkenyl groups. For example N-methyl-N,N,N-triethanolamine ditallowester or di-hardened-tallowester

25 quaternary ammonium chloride or methosulphate. Examples of commercially available TEA quats include Rewoquat WE18 and Rewoquat WE20, both partially unsaturated (ex. WITCO), Tetranyl AOT-1, fully saturated (ex. KAO) and Stepantex VP 85, fully saturated (ex. Stepan).

- 30 It is advantageous if the quaternary ammonium material is biologically biodegradable.

Preferred materials of this class such as 1,2-bis(hardened tallowoyloxy)-3-trimethylammonium propane chloride and their methods of preparation are, for example, described in US 4 137 180 (Lever Brothers Co). Preferably these materials

comprise small amounts of the corresponding monoester as described in US 4 137 180, for example, 1-hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane chloride.

- 5 Other useful cationic softening agents are alkyl pyridinium salts and substituted imidazoline species. Also useful are primary, secondary and tertiary amines and the condensation products of fatty acids with alkylpolyamines.

The compositions may alternatively or additionally contain water-soluble cationic fabric  
10 softeners, as described in GB 2 039 556B (Unilever).

The compositions may comprise a cationic fabric softening compound and an oil, for example as disclosed in EP-A-0829531.

- 15 The compositions may alternatively or additionally contain nonionic fabric softening agents such as lanolin and derivatives thereof.

Lecithins and other phospholipids are also suitable softening compounds.

- 20 In fabric softening compositions nonionic stabilising agent may be present. Suitable nonionic stabilising agents may be present such as linear C<sub>8</sub> to C<sub>22</sub> alcohols alkoxyated with 10 to 20 moles of alkylene oxide, C<sub>10</sub> to C<sub>20</sub> alcohols, or mixtures thereof. Other stabilising agents include the deflocculating polymers as described in EP 0415698A2 and EP 0458599 B1.

- 25 Advantageously the nonionic stabilising agent is a linear C<sub>8</sub> to C<sub>22</sub> alcohol alkoxyated with 10 to 20 moles of alkylene oxide. Preferably, the level of nonionic stabiliser is within the range from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight, most preferably from 1 to 4% by weight. The mole ratio of the quaternary ammonium  
30 compound and/or other cationic softening agent to the nonionic stabilising agent is suitably within the range from 40:1 to about 1:1, preferably within the range from 18:1 to about 3:1.

The composition can also contain fatty acids, for example C<sub>8</sub> to C<sub>24</sub> alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in particular, hardened tallow C<sub>16</sub> to C<sub>18</sub> fatty acids. Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by weight. Concentrated compositions may comprise from 0.5 to 20% by weight of fatty acid, more preferably 1% to 10% by weight. The weight ratio of quaternary ammonium material or other cationic softening agent to fatty acid material is preferably from 10:1 to 1:10.

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It is also possible to include certain mono-alkyl cationic surfactants which can be used in main-wash compositions for fabrics. Cationic surfactants that may be used include quaternary ammonium salts of the general formula  $R_1R_2R_3R_4N^+X^-$  wherein the R groups are long or short hydrocarbon chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a counter-ion (for example, compounds in which R<sub>1</sub> is a C<sub>8</sub>-C<sub>22</sub> alkyl group, preferably a C<sub>8</sub>-C<sub>10</sub> or C<sub>12</sub>-C<sub>14</sub> alkyl group, R<sub>2</sub> is a methyl group, and R<sub>3</sub> and R<sub>4</sub>, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).

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20 The choice of surface-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition. In fabric washing compositions, different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

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The total amount of surfactant present will also depend on the intended end use and may be as high as 60 wt%, for example, in a composition for washing fabrics by hand. In compositions for machine washing of fabrics, an amount of from 5 to 40 wt% is generally appropriate. Typically the compositions will comprise at least 2 wt% surfactant e.g. 2-60%, preferably 15-40% most preferably 25-35%.

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Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or non-ionic surfactant, or combinations of the two in any suitable ratio, optionally together with soap.

The compositions of the invention, when used as main wash fabric washing compositions, will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will typically range from 5 to 80 wt%, preferably from 10 to 60 wt%.

5 Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in  
10 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

15 The compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

20 The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula:  $0.8-1.5 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 0.8-6 \text{ SiO}_2$

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5  $\text{SiO}_2$  units (in the formula above). Both the amorphous and the crystalline  
25 materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

30 The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite  
35 MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to



aluminium weight ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

- 5 Especially preferred is zeolite MAP having a silicon to aluminium weight ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

- 10 Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di and trisuccinates, carboxymethyloxy succinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

- 15 Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

- 20 Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

- Compositions according to the invention may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxy bleach compounds, for  
25 example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.

- Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates,  
30 perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

- Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising  
35 sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

The peroxy bleach compound is suitably present in an amount of from 0.1 to 35 wt%, preferably from 0.5 to 25 wt%. The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt%, preferably from 0.5 to 5 wt%.

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxanoic acid precursors. Especially preferred bleach precursors suitable for use in the present invention are N,N,N',N'-tetracetyl ethylenediamine (TAED) and sodium nonanoyloxybenzene sulphonate (SNOBS). The novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company) and EP 402 971A (Unilever), and the cationic bleach precursors disclosed in EP 284 292A and EP 303 520A (Kao) are also of interest.

The bleach system can be either supplemented with or replaced by a peroxyacid. examples of such peracids can be found in US 4 686 063 and US 5 397 501 (Unilever). A preferred example is the imido peroxycarboxylic class of peracids described in EP A 325 288, EP A 349 940, DE 382 3172 and EP 325 289. A particularly preferred example is phthalimido peroxy caproic acid (PAP). Such peracids are suitably present at 0.1 - 12%, preferably 0.5 - 10%.

A bleach stabiliser (transition metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetra-acetate (EDTA), the polyphosphonates such as Dequest (Trade Mark) and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid). These bleach stabilisers are also useful for stain removal especially in products containing low levels of bleaching species or no bleaching species.

An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever).

The compositions according to the invention may also contain one or more enzyme(s).

Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions. Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They  
5 may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from  
10 particular strains of B. Subtilis B. licheniformis, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Genencor International N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novozymes Industri A/S, Copenhagen, Denmark.

15 Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novozymes Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark obtainable  
20 from Showa-Denko of Japan), Optimase (Trade Mark from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark obtainable from Pfizer of U.S.A.).

Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used.  
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The compositions of the invention may contain alkali metal, preferably sodium carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the  
30 scope of the invention.

Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate copolymer, or sodium silicate. One preferred powder structurant is fatty  
35 acid soap, suitably present in an amount of from 1 to 5 wt%.

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; soil release polymers; inorganic salts such as sodium sulphate; or lather boosters as appropriate; 5 proteolytic and lipolytic enzymes; dyes; coloured speckles; fluorescers and decoupling polymers. This list is not intended to be exhaustive. However, many of these ingredients will be better delivered as benefit agent groups in materials according to the first aspect of the invention.

- 10 The detergent composition when diluted in the wash liquor (during a typical wash cycle) will typically give a pH of the wash liquor from 7 to 10.5 for a main wash detergent.

15 Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or post-dosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

- 20 Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/l, more preferably at least 500 g/l. Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

25 Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used. Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

- 30 Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in compact form which means it will contain a lower level of water compared to a conventional liquid detergent.

### Product Forms

Product forms include powders, liquids, gels, tablets, any of which are optionally incorporated in a water-soluble or water dispersible sachet. The means for manufacturing any of the product forms are well known in the art. If the silicone and the substituted polysaccharide are to be incorporated in a powder (optionally the powder to be tableted), and whether or not pre-emulsified, they are optionally included in a separate granular component, e.g. also containing a water soluble organic or inorganic material, or in encapsulated form.

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### Substrate

The substrate may be any substrate onto which it is desirable to deposit silicones and impart a perfume thereto, and which is subjected to treatment such as a washing or rinsing process.

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In particular, the substrate may be a textile fabric. It has been found that particular good results are achieved when using a natural fabric substrate such as cotton, or fabric blends containing cotton.

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### Treatment

The treatment of the substrate with the material of the invention can be made by any suitable method such as washing, soaking or rinsing of the substrate.

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Typically the treatment will involve a washing or rinsing method such as treatment in the main wash or rinse cycle of a washing machine and involves contacting the substrate with an aqueous medium comprising the material of the invention.

30 The present invention will now be explained in more detail by reference to the following non-limiting examples:-

In the following examples where percentages are mentioned, this is to be understood as percentage by weight. In the following tables where the values do not add up to 100 these are to be understood as parts by weight.

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**Example A – Sample synthesis of an ester linked cellulose monoacetate (CMA) with grafted silicone**

- 5 Monocarboxydecyl terminated polydimethylsiloxane (PDMS) source (Mwt 5,000: 1.5g, 0.23 mmols) was dispersed in dimethylacetamide (10cm<sup>3</sup>) by vigorous stirring under nitrogen. Carbonyldiimidazole (37 mg, 0.23 mmols) was then added and the dispersion heated with stirring to 70°C under nitrogen for two hours. A solution of cellulose monoacetate (DS 0.58; 1 g, 5.3 mmol equivalents based on primary hydroxyl groups) in  
 10 dimethylacetamide (10 cm<sup>3</sup>) was then added and stirring and heating was continued for a further 20 hours. Following this time the mixture was filtered and the filtrate added to vigorously stirring acetone to give a white precipitate. This precipitate was filtered off, washed with acetone and dried under vacuum to give a white polymer (1.01g). From the <sup>1</sup>H NMR of the polymer (after hydrolysis of 20% DCI in D<sub>2</sub>O for two hours at 80°C) and  
 15 normalising the integration of the anomeric protons to unity and the acetate group to 0.58 the Si-CH<sub>3</sub> group (at 0.0 ppm) integration gives an overall degree of substitution (DS) of siloxane groups of 0.0015 (hereinafter referred to as "Polymer A").

**Example 1**

20

Model washes were done in 200ml, pots were prepared and treated as follows:-

- |    |         |   |  |
|----|---------|---|--|
| 25 | Per pot | - | 0.1 litre of wash liquor   |
|    |         | - | enough composition to give 3.0 mg silicone per gram of cotton                    |
|    |         | - | 1 piece of mercerised cotton 20 x 20 cm  |
|    |         | - | wash at 40°C for 30 mins, bottleshaker at shake speed of ~ 100 shakes per minute |
|    |         | - | rinse, 2 x 200ml tap water (nominal hardness 24°FH).                             |
| 30 |         |   | Fabric dried o/n on a flat surface of ambient temperature                        |

The wash liquor for example 1 and the control were as follows:

Ingredient	Quantity g/L in H <sub>2</sub> O	
	Example 1	Control
Wash Liquor		
NaCl	0.6	0.6
Sodium Tripolyphosphate	0.66	0.66
Na <sub>2</sub> CO <sub>3</sub>	0.75	0.75
Na alkyl benzene sulphonate	0.6	0.6
Nonionic*	0.19	0.19
<b>Preformed Emulsion (2% in H<sub>2</sub>O)</b>		
Nonionic**	0.009	0.009
PDMS***	0.18	0.18
Polymer A	0.018 (post dosed)	-

5. \* Average C<sub>10</sub> fatty alcohol ethoxylated with an average of 6 ethylene oxide units.

\*\* Synperonic A7, nonionic surfactant ex shell.

\*\*\* The polydimethylsiloxane (PDMS) silicone oil was pre-mixed with a proprietary detergent powder perfume in a weight ratio of 20:1 of PDMS:perfume.

10 Fabrics were then analysed for silicone depositing according to the following protocol:

- Solvent extraction of silicones from fabric. Use 10 ml THF/g of cotton
  - extract at room temperature for 24 hrs with constant agitation.
  - analyse THF for silicone levels via gel permeation chromatography (GPC), using
- 15 evaporative light scattering detector.

An analogous method was used to detect perfume deposition.

The deposition analysis gave the following results

Results Target dose = 3 mg/g

Silicone	% deposit
Control	5.49
Example 1	33.7

5

Perfume	% deposit (units)
Control	667
Example 1	1084

Raw material specification:

Component	Specification
Polymer A	Material Specified in Example A.
Nonionic** (as above)	A nonionic surfactant.....